Role of the activity coefficient in the dissemination of pH:comparison of primary (Harned cell) and secondary (glass electrode)measurements on phosphate buffer considering activityand concentration scales

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ORIGINAL PAPER

Paola Fisicaro · Enzo Ferrara · Enrico Prenesti
Silvia Berto

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Abstract Despite recent efforts devoted to assessing both the theoretical rationale and the experimental strategy for assignment of primary pH values, these have not yet been accomplished satisfactorily. Traceability and comparability of pH values are achieved only within the constraints of internationally accepted conventions and predefined conditions that cannot account for all possible situations when pH is measured. Critical parameters to be defined are, in particular, the activity coefficients (γ_i) of the ionic species involved in the equilibrium with the hydrogen ions in the solution, which are usually estimated with the approximation typical of the Debye–Hückel theoretical model. For this paper, primary (Harned cell) measurements (traceable to the SI system) of the pH of a phosphate buffer have been considered and the results have been compared with secondary (glass electrode) measurements obtained by considering either the activity (p*a*H) or concentration (p*c*H) scale of the hydrogen ions. With conventional approaches based on measurements related to activity or concentration scale, discrepancies emerge which have been assigned to incomplete inferences of γ_i arising from chemical features of the solution. It is shown that fitting and comparable p*a*H and p*c*H results are attainable if evaluation of γ_i is performed using better estimates of the ionic strength, according to an enhanced application of the Debye–Hückel theory.

Keywords Primary pH measurement · Activity coefficients · Phosphate buffer · Ionic strength · Ionic medium

P. Fisicaro (✉) · E. Ferrara
Istituto Elettrotecnico Nazionale Galileo Ferraris,
Strada delle Cacce 91, 10135 Torino, Italy
E-mail: fisicaro@ien.it

E. Prenesti · S. Berto
Dipartimento di Chimica Analitica dell'Università,
via Pietro Giuria 5, 10125 Torino, Italy

Introduction

The concept of pH is very special in the field of physicochemical quantities, because of its widespread use as an important control property and process descriptor and because of the difficulty of defining its theoretical meaning. Its definition involves the activity of a single ion [1], which, according to the rules of thermodynamics, cannot be inferred alone in practice. To bypass this point, several experimental details related to the primary measurement of pH have been carefully and extensively developed and discussed along with a series of theoretical considerations of thermodynamics [1–6]. Unfortunately, the overall accuracy of currently established methodology suffers because of the approximate nature of some general assumptions, which leads to difficulties in comparison when properties of the solutions such as ionic strength and ionic medium are changed. In this context, recent IUPAC recommendations [1] emphasized the need for careful inspection of the reference model used to calculate the activity coefficients of the ions, even beyond the Bates–Guggenheim convention. In fact, scientists regarded the Bates–Guggenheim convention as an axiomatic tool, whereas additional attention might be fruitfully focused on the correct choice of ionic activity coefficients (γ_i) to avoid losses in the accuracy attainable with modern powerful experimental apparatus.

To overcome the limitations and incoherencies of the Bates–Guggenheim convention, we propose in this paper an analysis of a series of comparative experiments supported by modifications of the theoretical approach to activity coefficients, which was the outcome of our tests and reflections. The final aims are:

1. improvement of the agreement between primary (Harned cell) and glass electrode measurements of pH, and
2. achievement of better harmonization for this fundamental quantity of chemistry [7], control of

which is ubiquitously pursued in scientific applications to monitor both natural and industrial processes.

In this work, primary measurement of the pH value of a phosphate buffer was performed by using the Harned cell, together with the critical estimation of the properties related to the electrolytic composition of the solution which significantly affect the final result. To expand the study we also considered pH measurement using an indicating device as glass electrode (secondary pH measurement). The outcomes have been compared to check whether discrepancies increase as a result of evaluation of E° by use of either:

1. standard pH-metric reference solutions (calibration in activity scale), as usually performed in most of the chemical and biochemical laboratories, or
2. acid–base titration supplying pH values (concentration scale), as typical of the experimental framework followed for formation constant refinement from potentiometric data [8, 9].

Besides classical procedures [1], preliminary evaluation of E° has also been performed using two background electrolytes, KCl or $NaClO_4$, to verify the sensitivity of our potentiometric apparatuses with regard to different ionic strength and media. Three temperatures were tested, 288.15, 298.15, and 310.15 K, in primary measurements, whereas use of the glass electrode was performed at 298.15 K only, because in the thermodynamics literature 298.15 K is the reference temperature [10] and usual laboratory practice is to operate at room temperature.

For calculation of the activity coefficients at different ionic strength we used a Debye–Hückel type equation [11] with a tested high level of accuracy. The value of the activity coefficient was revealed to be a source of discrepancy between pH values obtained from activity or concentration scales. We believe it is appropriate to exploit the matching of the results originating from use of different measurement methods leading to paH evaluation, if the thermodynamics equations applied are adequate for the level of accuracy required. Consistency between Harned cell (activity scale) and glass electrode (concentration scale) outputs can be improved by calculating the activity coefficients according to a reference model faithfully corresponding to the exact properties of the test solutions.

Experimental

Symbols

paH is used to indicate the quantity expressed on the activity scale ($paH = -\log a_H$); pcH is used to indicate the quantity expressed on the concentration scale ($pcH = -\log[H^+]$).

Chemicals

Disodium hydrogen orthophosphate (Na_2HPO_4, 99.0%, Merck) and potassium dihydrogen orthophosphate (KH_2PO_4, 99.5%, Merck) were used to prepare the 0.05 mol kg^{-1} phosphate buffers. A 30% HCl solution in water (Merck) was used to prepare the 0.01 mol kg^{-1} HCl solution used to evaluate the standard potential difference of the primary cell (E°). Pure potassium chloride (KCl, 99.995%, Merck) was used as background salt (primary and secondary procedures). Phosphate (paH 6.98 ± 0.02, Merck) and citrate (paH 2.00 ± 0.02, Merck) buffers were used to calibrate the glass electrode at 298.15 K. Standard solutions of NaOH and HCl were prepared by diluting concentrated Merck solutions from ampules and were standardized against potassium hydrogen phthalate or sodium carbonate, respectively. All the solutions were prepared using deionized and doubly distilled water in grade-A glassware. $NaClO_4$ (anhydrous, >99%) was from Sigma.

Primary potentiometric apparatus (Harned cell)

The Harned cell [12] has been considered as a means of gaining international acceptance of a thermodynamics-based procedure for pH measurement. It consists of two symmetrical semi-cells containing the hydrogen working electrode and the silver–silver chloride reference electrode, respectively. The hydrogen electrode is made of a platinum plate immersed in the semi-cell in which pure H_2 gas flows, saturating the solution. The reference electrode is made of a platinum wire coated with metallic Ag and AgCl salt. The cell is immersed in a 7005 Hart Scientific thermostatic bath (± 0.001 K) and the potential difference (E) between the electrodes is quantified with a 34401A Agilent digital multimeter (resolution ± 0.001 mV).

The complete cell is usually represented schematically as follows:

$$Pt|H_2|\text{buffer solution}, Cl^-|AgCl|Ag$$

With this device, definition as a ''primary method of measurement'' traceable to the International System of Units (SI) (i.e., without the need to relate results to additional references for the same unit) is applicable for potentiometric inference of paH [1].

Experimental procedure with the primary cell

The term paH is conventionally defined as the negative logarithm of the activity (a) of the hydrogen ion: $paH = -\log a_H$. In aqueous solutions, the activity (a) and concentration (m) for a single ion (i) are associated by the activity coefficient (γ_i). When the molal concentration is expressed as m in mol kg^{-1} and the standard

Table 1 Experimentally obtained acidity function extrapolated to zero chloride concentration $p(a_H\gamma_{Cl})^\circ$, the activity coefficient of chloride ion, $\log(\gamma_{Cl})^\circ$, and the resulting p*a*H from measurements on phosphate buffer at three temperatures (288.15, 298.15, and 310.15 K). E° evaluation conditions: HCl 0.01 mol kg^{-1}

Quantity	$T = 288.15$ K	$T = 298.15$ K	$T = 310.15$ K
$p(a_H\gamma_{Cl})^\circ$	6.994	6.957	6.938
$\log(\gamma_{Cl})^\circ$ [a]	−0.1078	−0.1095	−0.1119
p*a*H	6.887	6.847	6.825

[a]Conventionally calculated according to IUPAC recommendations [1]

molal concentration for the hydrogen ion (H^+) as $m^\circ = 1$ mol kg^{-1}, then $a_H = \gamma_H m_H/m^\circ$. When the Harned cell is employed in solution, the following equilibrium must be considered:

$$\tfrac{1}{2}\,H_{2\,(g)} + AgCl_{\,(s)} \rightleftharpoons Ag_{\,(s)} + H^+ + Cl^- \qquad (1)$$

On application of the Nernst equation to Eq. 1, the potential difference between the electrodes is described as depending on the ionic activities in the solution:

$$E_I = E^\circ - [(RT/F)\ln 10]\log[(m_H\gamma_H/m^\circ)(m_{Cl}\gamma_{Cl}/m^\circ)] \qquad (2)$$

where E_I is the potential difference (corrected to 101.325 KP_a hydrogen partial pressure using the corrective factor from ref. [2]); E° is the standard potential difference of the cell; m_H and m_{Cl} are the molal concentrations of the ionic species, and γ_H and γ_{Cl} are the activity coefficients of the single ions.

Before measurement of the buffer, the standard potential difference (E°) of the cell must be separately determined experimentally. A standard solution of HCl was therefore measured in the Harned cell. In this case we assume $m_H = m_{Cl}$, and $\gamma_{\pm HCl}$ is the average activity coefficient of the ions in the HCl solutions, the recommended value of which is 0.904 ($I = 0.01$ mol kg^{-1}, $T = 298.15$ K, see also Table 1) [1]. Appropriate γ_i values were used in this paper when working at $I = 0.1$ mol kg^{-1} (see "Results and discussion" and Tables 2 and 3). In the conventional procedure [1], Nernst Eq. (2) can be reduced to:

$$E_I = E^\circ - [2(RT\ln 10/F)]\log(m_{HCl}\gamma_{\pm HCl}) \qquad (3)$$

For assessment of p*a*H for the phosphate buffer, the potential E has been measured for four phosphate solutions by adding different amounts of KCl, corresponding to 2.50×10^{-3}, 5.00×10^{-3}, 1.00×10^{-2}, and 1.50×10^{-2} mol kg^{-1}. Rearranging Eq. 2 gives an empirical term, $p(a_H\gamma_{Cl})$, which is called the acidity function and is considered to be mainly dependent on the chloride concentration:

$$p(a_H\gamma_{Cl}) = -\log(a_H\gamma_{Cl}) = (E_I - E^\circ)/[(RT/F)\ln 10] + \log(m_{Cl}/m^\circ) \qquad (4)$$

As an example, the experimental results plotted in Fig. 1 give the values of $p(a_H\gamma_{Cl})$ as a function of the added chloride and temperature; the experimental readings of potential are the average values after the solution reached equilibrium temperature and gas flow conditions. Measurements are repeated at least twice for each series. Extrapolating the lines of best fit, the acidity function at zero chloride molality, $p(a_H\gamma_{Cl})^\circ$, is obtained for each temperature. A test at 2.50×10^{-3} mol kg^{-1} chloride ion was also used to reduce the arbitrary character of the extrapolation; even if low in KCl concentration, this measure provided readings as meaningful and accurate as others in the series.

By extrapolating the data to zero chloride concentration (Fig. 1), the term $p(a_H\gamma_{Cl})^\circ$ is obtained, according to a procedure based on the specific ion interaction theory [13, 14]. Finally, to evaluate the p*a*H of the buffer, the following calculation is used:

$$pa_H = -\log a_H = p(a_H\gamma_{Cl})^\circ + \log(\gamma_{Cl})^\circ \qquad (5)$$

$(\gamma_{Cl})^\circ$ is independently calculated from the extended Debye–Hückel equation valid for aqueous solutions with low ionic strength, namely, $I \le 0.01$ mol kg^{-1}. The Bates–Guggenheim convention (BG) [15] enables the following equation to be used to estimate $(\gamma_{Cl})^\circ$:

$$\log(\gamma_{Cl})^\circ = -\frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} \qquad (6)$$

where A is a temperature-dependent term. At 298.15 K, for $I = 0.1$ mol kg^{-1}, $\log(\gamma_{Cl})^\circ = -0.1095$.

Secondary potentiometric apparatus

The potentiometric measurements of p*a*H were performed at $T = (298.15 \pm 0.10)$ K and $I = 0.1$ mol kg^{-1} (KCl or $NaClO_4$) by means of a Metrohm 713 potentiometer (resolution ±0.1 mV) equipped with a combined glass electrode provided by Metrohm (Switzerland), mod. 6.0222.100, internal Ag/AgCl reference electrode (filling electrolyte 3 mol L^{-1} KCl), ceramic single junction (electrolyte flow in the range 15–20 μL h^{-1}). The titrant, a standardized solution of KOH, was dispensed

Table 2 Step by step calculation of the activity coefficient γ_i for a singly charged ion (Eq. 9)

I	$\sqrt{I}$	$z^2_i\sqrt{I}\cdot(2 + 3\sqrt{I})^{-1}$	CI	$-DI^{3/2}$	γ_i
0.1	0.3162	0.1072	0.033 ± 0.005[a]	0.0032 ± 0.0003[a]	0.837 ± 0.010[a]

[a]The range (value ± standard deviation) is estimated from the uncertainty of the coefficients in Eq. 8

Table 3 Extrapolated data of the acidity function at zero chloride concentration for three temperatures and two ionic strength values, and the corresponding p*a*H

$E°$ conditions	Quantity	$T = 288.15$ K	$T = 298.15$ K	$T = 310.15$ K
$I_{HCl} = 0.01$ mol kg^{-1}	$p(a_H\gamma_{Cl})°$	6.994[a]	6.957[b]	6.938[c]
	p*a*H	6.921[d]	6.879[e]	6.853[f]
$I_{HCl+KCl} = 0.10$ mol kg^{-1}	$p(a_H\gamma_{Cl})°$	6.995[g]	6.956[h]	6.940[i]
	p*a*H	6.922[d]	6.879[e]	6.855 [f]
$I_{HCl+NaClO4} = 0.10$ mol kg^{-1}	$p(a_H\gamma_{Cl})°$	6.978[g]	6.942[h]	6.927[i]
	p*a*H	6.904[d]	6.865[e]	6.843[f]

γ_{Cl} values: [d]0.845; [e]0.837; [f]0.823
$\gamma_{\pm}$ values: [a]0.9060, [b]0.9042, [c]0.9020, [g]0.8000, [h]0.7964, [i] 0.7907

with a 765 Dosimat Metrohm burette (minimum deliverable volume 0.001 cm^3). Temperature control was achieved by water circulation in the outer chamber of the titration cell, delivered by a Haake model D1-G thermo cryostat.

Measurement in activity scale

Certified p*a*H-metric buffers traceable to NIST (National Institute of Standard and Technology), corresponding to p*a*H = 2.00 and p*a*H = 6.98, were used to calibrate the electrode couple (glass electrode) at 298.15 K, according to the activity scale.

Measurement in concentration scale

Before measurement the electrode couple was used to obtain $E°$ at 298.15 K by application of the Nernst equation in terms of concentration (p*c*H = −log [H$^+$]). Alkalimetric titration with standard carbonate-free KOH was previously employed, under a stream of purified nitrogen gently bubbled in the cell to avoid O_2 and CO_2 dissolution, to determine HCl concentration (mmol kg^{-1} level). The ionic strength of the calibrating solutions was maintained consistent with the specimens under examination. Each titration was repeated at least twice.

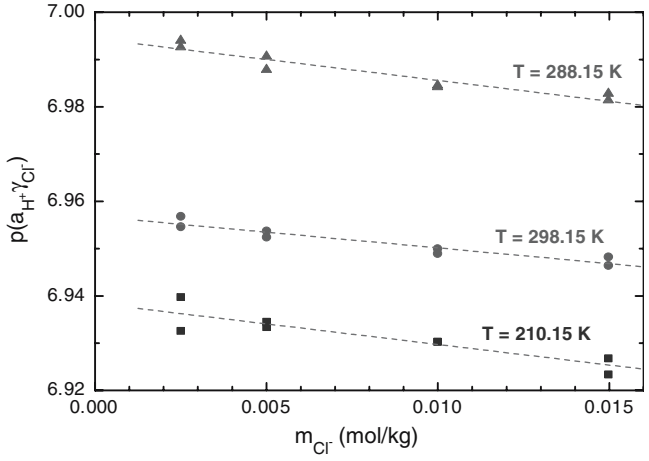

Fig. 1 Acidity function $p(a_H\gamma_{Cl})$ as a function of the added chloride for the phosphate buffer at 288.15, 298.15, and 310.15 K. The following relationship is assumed [1]: $-\log(a_H\gamma_{Cl}) = -\log(a_H\gamma_{Cl})° - S\, m_{Cl}$

Data analysis and calculations

The nonlinear least-squares computer program ESAB2M was used to evaluate the purity of the reagents (starting from acid–base titration data) and to refine all the data related to the evaluation of $E°$ for the glass electrode system [16]. This program allows refinement of the analytical concentration of reagents (the strong acid, in this context), the electrode formal potential $E°$, the coefficient j_a relative to the junction potential (where $E_j = j_a$ [H$^+$]) [8, 9], and the ionic product of water K_w. The slope for the glass electrode is considered to be equal to 59.16 mV at 298.15 K. The operator is allowed to choose the set of data to be refined in each job. In particular, we verified the influence of j_a around neutrality and found it was close to zero.

The standard uncertainty, u(pH), of measurements with the glass electrode is currently quantified in the range 0.01–0.03 [1, 17, 18] according to various experimental results.

Calculations of linear fits and overall uncertainty estimates were performed by means of standard commercial software.

Ionic strength and activity coefficient calculation

Usually, in literature concerning the primary measurement of pH, each ionic activity coefficient (γ_i) is calculated according to the extended Debye–Hückel equation:

$$\log \gamma_i = -\frac{Az_i^2\sqrt{I}}{1 + \mathring{a}B\sqrt{I}} \qquad (7)$$

where $A = 0.509$ at 298.15 K, z is the electrical charge of ion i, $\mathring{a}$ is the radius of the aqueous ion, and $B = 0.33\times10^{10}$ m^{-1} at 298.15 K.

Some constraints affect the limit of the Debye–Hückel equation, including the arbitrary linearization of the Poisson–Boltzmann equation. It is recognized that the extended Debye–Hückel equation provides accurate

result for γ_i only when $I \leq 0.01$ mol L^{-1}. Hence, use of the extended Debye–Hückel equation under the chemical conditions investigated in this paper is substantially incorrect, because the overall ionic strength of the testing solution (phosphate buffer) is close to 0.1 mol kg^{-1}, as obtained according to the so-called self-medium technique (and as one can estimate by considering the protonation constants of the hydrogen phosphate ion and the p*a*H value of the solution). Consequently, extended calculation models for γ_i must be considered according to an experimental design that should enable more reliable results to be obtained. With this objective we started using a Debye–Hückel type equation widely discussed elsewhere [19]. This equation enables calculation of activity coefficients at different ionic strengths in the range $0 \leq I \leq 1$ mol L^{-1}:

$$\log \gamma_i = -z_i^2 A \frac{\sqrt{I}}{1 + B\sqrt{I}} + CI + DI^{\frac{3}{2}} \quad (8)$$

where $A = 0.5$, $B = 1.5$, $C = c_0 + c_1 z_1^2$, and $D = -d_1 z_1^2$; z is the electrical charge.

In Eq. 8, we have (298.15 K): $c_0 = 0.10 \pm 0.03$, $c_1 = 0.23 \pm 0.02$, $d_1 = -0.10 \pm 0.01$ (uncertainties were estimated in ref. [20]). Then, assuming for A and B the values quoted we obtain:

$$\log \gamma_i = -z_i^2 \frac{\sqrt{I}}{2 + 3\sqrt{I}} + CI + DI^{\frac{3}{2}} \quad (9)$$

The terms involved in the assessment of C and D have been estimated for a very large number of inorganic and organic electrolytes [11, 19–21].

Results and discussion

Activity coefficients

In Table 2 calculation of the activity coefficient (γ_i) for a singly charged ion (H^+ or Cl^- in our context) is reported step by step to clarify the contribution of each term.

Using Eq. 7, at $I = 0.1$ mol kg^{-1} and 298.15 K, a value of $\gamma_i = 0.777$ is obtained, whereas by using Eq. 9 we calculated $\gamma_i = 0.837$ (Table 2), which is in excellent agreement with the findings in ref. [11], where a recommended value of 0.839 ± 0.0061 is reported for γ_i for the H^+ ion at 298.15 K and $I = 0.09$ mol kg^{-1}; this value was obtained as an average from a wide set of work based on the same theory as that used to estimate $\gamma_i = 0.837$.

Primary method according to IUPAC recommended approach

Two series of measurements were performed with the primary Harned cell. The experimental results are plotted in Fig. 1, which reports the values of $p(a_H \gamma_{Cl})$ as a function of added chloride and temperature. Numerical results are collected in Table 1.

Primary method: determination of E° with KCl or $NaClO_4$ added

For this work, the 0.01 mol kg^{-1} HCl solution usually used for E° evaluation was modified in composition by adding KCl or $NaClO_4$ in amounts giving an ionic strength of 0.1 mol kg^{-1}, which is consistent with the buffer sample. Two different salts were used to verify the robustness of the apparatus with regard to electrode-sensitive (Cl^-) and electrode-insensitive (ClO_4^-) ions. The Harned cell, responds reversibly to the chloride activity, while KCl addition adjusts the ionic strength of the solution. The measured potentials (298.15 K) correctly account for these important variations of the chemical features of the solution: $E_{HCl} = 465.13$ mV, $E_{HCl+KCl} = 408.94$ mV, $E_{HCl+NaClO4} = 471.42$ mV. These changes enable the response of the method to be checked in accordance with the applied rules of thermodynamics, indicating how chemical modification of the sample can affect the overall procedure.

The important variations of ionic strength imposed on the system under investigation force us to find suitable values of $\gamma_{\pm HCl}$ to calculate E°. For estimation of $\gamma_{\pm HCl}$ at $I = 0.1$ mol kg^{-1} we used the values given by Harned and Owen [12]: at 288.15 K $\gamma_{\pm HCl} = 0.8000$, and 298.15 K $\gamma_{\pm HCl} = 0.7964$; at 310.15 K $\gamma_{\pm HCl} = 0.7907$ was obtained by linear interpolation of the values reported between 308.15 K (0.7918) and 313.15 K (0.7891). Excellent agreement is found for $\gamma_{\pm HCl}$ at $I = 0.1$ mol kg^{-1} and $T = 298.15$ K as reported by Harned and Owen (0.7964) [12] and Robinson (0.796) [22]. Table 3 collects the acidity functions extrapolated to zero chloride according to chosen temperatures, ionic strengths, and ionic media.

Secondary method: glass electrode and calibration with p*a*H-metric buffers

The measurement performed on the phosphate buffer with a glass electrode at 298.15 K, after calibration with reference p*a*H buffer solutions, yielded a value equal to 6.85 (averaged value from triplicate measurements).

Secondary method: glass electrode and evaluation of E° in concentration

Optimization of E° was performed by titrating a solution of HCl at 298.15 K with standard KOH. The ionic strength was adjusted to 0.1 mol kg^{-1} with KCl or $NaClO_4$. The measurement is performed following the variation of the potential by the glass electrode. This yields E° and p*c*H of the testing solution (phosphate buffer) in terms of concentration.

Choice of γ_i values

When the acidity function and the pcH in concentration have to be converted in terms of paH, choice of the appropriate γ_i value is necessary. As previously described, scientists in the past promoted a variety of theoretical approaches for evaluation of activity coefficients and this resulted in a tangled mass of papers, sometimes contradictory. The activity coefficients of ions in aqueous solution have been shown to depend on many variables, in particular temperature, ionic medium (nature of the background salt), and ionic strength. The reference model adopted to describe the chemistry of the electrolytic solutions and then used to calculate the dependence of thermodynamic quantities on ionic strength is critical and together with other variables (see below) accounts for the wide range of values available in the literature. An unambiguous value of γ_i probably cannot be found, because extra-thermodynamic assumptions are unavoidable to obtain the desired term and results are often technique-dependent. Moreover, besides extra-thermodynamic assumptions, several theoretical, empirical, and semi-empirical equations are used to process experimental data or to obtain ab initio based values of γ_i. What is also remarkable and interesting is the dependence of γ_i on the nature of the background electrolyte used to fix the ionic strength (if self-medium behavior is not adopted).

Two series of equations for γ_i calculation developed according to chemical or physicochemical models can be identified:

- Many papers regarded each ion as characterized by its charge (according to the original Debye–Hückel theory) and found a strategy to optimize a value of γ_i only dependent on the ionic strength; specificity factors are neglected but the coefficients of the semi-empirical Debye–Hückel type equation—optimized by calculations on a large amount of experimental data—enable smoothed and averaged values to be obtained. Fruitful applicability of this choice can be predicted for environmental, clinical, geological, and biological chemistry, for example, where multi-component systems are examined;
- In other papers [23–25] in which γ_i values are evaluated, efforts are pursued considering each single ion with its chemical character, leading to a wide set of specific interaction coefficients depending on physicochemical variables.

Values of γ_i suitable for a predetermined chemical environment of particular meaning can be regarded as very useful, especially when pH is applied in the study of the stability constants of aqueous solutions, whose refinement is always performed starting with data collected for synthetic solutions [7]. Otherwise, average values of γ_i suitable to fit different experimental scenarios can also be seriously considered for their ability to describe important properties of the ions when inserted in a complex context. The power of the model chosen will be limited by assumptions about γ_i, but the wideness and the generality of the description will be enriched by the availability of averaged thermodynamic data. Fortunately, the ionic strength considered in this paper, 0.1 mol kg^{-1}, corresponding to a low slope of the $\log\gamma_i/\sqrt{I}$ curve, enables exclusion of errors that could introduce bias in the mean γ_i values adopted. If we consider higher ionic strength values the slope of the $\log\gamma_i/\sqrt{I}$ curve increases and the chemical assumptions related to the ionic interactions in solution become fundamental to correct calculation of the activity coefficient.

Acidity function conversion to paH

paH values in Table 1 have been evaluated by subtracting from $p(a_H\gamma_{Cl})^\circ$ the ionic chloride coefficient, $\log(\gamma_{Cl})^\circ$, calculated according to the conventional terms of the extended Debye–Hückel equation (BG convention).

Table 4 Comparison of paH (activity scale) and pcH (concentration scale) values obtained with the primary Harned cell and the glass electrode, respectively, at 298.15 K using different activity coefficients

Apparatus	Quantity	Measurement conditions		
		A[a]	B[b]	C[c]
Harned cell	$p(a_H\gamma_{Cl})^\circ$	6.957	6.956	6.942
Glass electrode	pcH	6.80	6.76	6.79
		$\gamma_i = 0.777$		
Harned cell	paH	6.847[d]	6.846[d]	6.832[d]
Glass electrode	paH	6.91[e]	6.87[e]	6.90[e]
		$\gamma_i = 0.837$		
Harned cell	paH	6.879[d]	6.879[d]	6.865[d]
Glass electrode	paH	6.88[e]	6.84[e]	6.87[e]

[a] E° evaluated in solutions containing HCl 0.01 mol kg^{-1} ($I = 0.01$ mol kg^{-1})
[b] E° evaluated in solutions containing HCl 0.01 mol kg^{-1} and KCl 0.09 mol kg^{-1} ($I = 0.1$ mol kg^{-1})
[c] E° evaluated in solutions containing HCl 0.01 mol kg^{-1} and $NaClO_4$ 0.09 mol kg^{-1} ($I = 0.1$ mol kg^{-1})
[d] Calculation of paH from $p(a_H\gamma_{Cl})^\circ$ performed using the signed coefficient
[e] Calculation of paH from pcH performed using the signed coefficient

pcH conversion to paH

pcH can be easily converted to paH by considering the appropriate activity coefficient γ_H. Results are collected in Table 4, using two values of γ_H selected according to the previous considerations.

paH can also be obtained by direct calibration via paH-metric buffers (the usual laboratory practice). Results on activity scale from primary—paH = 6.847 ($\gamma_i = 0.777$)—and secondary—paH = 6.85—devices reveal a very satisfactory agreement, as expected.

A different situation is obtained when primary paH values are compared with those of the glass electrode based on a concentration scale and obtained with the conventionally adopted activity coefficient ($\gamma_i = 0.777$) (see Table 4, upper part). Fortunately, the observed discrepancies can be overcome if the appropriate activity coefficient is applied (lower part of Table 4, $\gamma_i = 0.837$).

Let us examine the results related to measurement conditions *B* and *C* in Table 4 and $\gamma_i = 0.837$. Outputs from the Harned cell show very small dependence on ionic strength and ionic medium. These results clearly indicate the ability of the calculations to take into account the variation of *I* obtained with KCl. As far as results obtained with a glass electrode are concerned, dependence on both *I* and the nature of the background electrolyte [26] is found, as expected. As for the comparison between primary and secondary apparatuses, it is clear that measurement conditions for both *A* and *C* type lead to better comparability, which is fundamental for dissemination purposes.

In Table 3 the extrapolated data of the acidity function at zero chloride concentration are collected for different temperature and ionic strength, along with the corresponding paH. For γ_{Cl} calculation at $I = 0.1$ mol kg^{-1} we used Eq. 9; the coefficients c_0, c_1, and d_1 are those in ref. [19] at 298.15 and 310.15 K, whereas for 288.15 K we exploited the relationships linking the coefficients with temperature in the range 283.15–318.15 K. We obtained $\gamma_{Cl} = 0.845$ at 288.15 K, and $\gamma_{Cl} = 0.823$ at 310.15 K.

Contribution to the evaluation of uncertainty

The expanded uncertainty *U* of primary paH determination is quantified in this paper as $U = \Delta pH = 0.006$ (at 298.15 K for the solution containing 0.005 mol kg^{-1} KCl). This value has been obtained by multiplying the standard uncertainty of the measurement for a coverage factor $k = 2$, which accounts for a level of confidence of 95%. The calculations are performed in accordance with published procedures [1, 27]. The calculated expanded uncertainty does not include the uncertainty which results from using the BG convention. But, to obtain paH measurements traceable to the SI system, an estimate of the uncertainty contribution of each step must be included in the result. An attempt has been made [1] to estimate the range of variability of the $(\gamma_{Cl})^\circ$ value. Varying the coefficient $\mathring{a}B$ in Eq. 6 between 1.0 and 2.0 (mol kg^{-1})$^{1/2}$, the $(\gamma_{Cl})^\circ$ value is affected by a variability of ± 0.012 at $I = 0.1$ mol kg^{-1}. This corresponds to varying the ion-size parameter in the range 0.3–0.6 nm [1].

Starting from the standard deviation associated with the coefficients in Eq. 8 and estimated on the basis of a very wide set of thermodynamic data of stability constants, at various ionic strength values, the γ_i term (calculated from Eq. 9) varies between 0.827 and 0.847 (Table 2). This standard uncertainty remains within ± 0.010 paH units.

Conclusions

In this paper we assumed $\gamma_{Cl} = \gamma_H$ as a tool of comparison to obtain paH values from various experimental sources. This assumption is coherent with the reference model for calculation of γ_i (i = positive or negative charge) and is in agreement with the IUPAC recommendation [1] for handling hydrogen ion concentration.

We can conclude by observing that conventional values of chloride ion activity coefficients which are adopted worldwide and applied for primary and secondary paH measurements can be further improved according to the theory of thermodynamics that better describes the property of solutions. Improvement of agreement between primary (Harned cell) and secondary (glass electrode) measurements of paH can be achieved to ensure a higher level of harmonization and dissemination for this fundamental quantity, control of which is performed in a variety of scientific and technological applications to monitor natural, clinical, and industrial processes.

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